

Laser Ignition in Self-Propagating High Temperature Synthesis of Porous NiTi₂ Shape Memory Alloy

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Abstract

Self-propagating High temperature Synthesis (SHS) is a challenging method for producing porous near net-shape materials. Starting from pure metallic powders several compounds can be fast synthesized. Among promising porous structured materials for biomedical applications NiTi₂ Shape Memory Alloy can be suitable for their peculiar properties, like shape memory effect or pseudo-elasticity, high biocompatibility and lightness.

In the present work SHS process on Ni and Ti elemental powders, ignited by a laser beam, was studied. The effect of main laser parameters (laser power and exposition time) was studied on porosity, microstructure and martensitic transformation temperatures. Samples with porosity in the range 42-48% were produced; NiTi matrix and other secondary phases, like NiTi₂, Ni₃Ti and Ni₄Ti₃ were detected. No dependence of microstructure and transformation temperatures with the process parameters was found.

Keywords: Porous NiTi₂, SMA, SHS process, laser ignition.

Introduction

Shape Memory Alloys (SMAs) have been received a world-wide interest due to their excellent properties, namely shape memory effect and pseudoelasticity [1]. Among SMAs, porous NiTi SMAs have been characterized from high biocompatibility and high corrosion resistance [2]. Furthermore, the porous structure of NiTi is beneficial for new bone tissue ingrowth and vascularization since, depending of porosity characteristics [3], the material presents high permeability to body fluids [4].

Self-Propagating High temperature Synthesis (SHS) is one of the most attractive methods for producing porous NiTi [5-6]. This method is based on exothermic combustion reaction of elemental Ni and Ti powders [7], occurring in four main steps: preheating, ignition, front propagation and cooling [8-9].

Preheating is required when the combustion reaction is not sufficiently exothermic, as in the case of Ni with Ti, and consequently additional heat has to be provided to the reacting mixture [10-

11]. The reaction then occurs once the powder temperature reaches the so called ignition temperature; ignition can be done by several methodologies, such as laser radiation, resistance heating coil and radiant flux [12]. The advantages of using a laser beam are easy control of the heating, high repeatability and non-contact heat transfer process.

The heat released from this first reaction is then transferred along the compact and the combustion becomes self-propagating [13-14]. Literature on NiTi produced by SHS reveals a strong influence of preheating temperature and ignition mode on the pore shape and size. The control of preheating is fundamental; if temperatures higher than necessary does not permit the synthesis of the porous structure [15].

In this work laser ignition in SHS of porous Nitinol samples was studied. The definition of the sufficient energy for SHS ignition is of great importance, hence the effect of laser power and exposition time on the feasibility area, porosity value and morphology, microstructure and calorimetric properties of porous samples was investigated.

Experimental

Elemental Ni (99.99% purity, size range of 3-7 μm) and Ti (99.7% purity, size of 149 μm) powders, from Sigma-Aldrich producer, were mixed for obtaining an equiatomic Ni-Ti mixture under argon atmosphere. Powder mixture was put into a cylindrical glass vial (inner diameter of 12 mm and height of 44 mm) and then gently pressed with a pressure of 3 MPa to obtain homogenous pellets.

The SHS apparatus was characterized by a laser source and a stainless steel combustion chamber. A diode laser (mod. Laserwave LW301250-980), having maximum power of 250 W, was used in the experiments. The combustion chamber is connected to vacuum pump and Ar supplier to make the process under inert atmosphere. Details of the experimental SHS apparatus are reported elsewhere [2-3].

The experiments were performed using a complete factorial design for investigating the laser power (100-150-200 W) and exposition time (0.4-0.6-0.9 s) at fixed preheating temperature of 350°C [16].

Morphology and chemical composition of porous samples were studied by means of optical and scanning electron microscopy (SEM, mod. HITACHI SU-70), coupled with energy dispersive X-ray spectroscopy (EDX), respectively. X-Rays diffraction analysis was done for the identification of the phases using a diffractometer (mod. X'Pert PRO) at room temperature. Transformation temperatures were measured by differential scanning calorimetry (DSC, mod. SEIKO SSC/5200) with 10°C/min heating/cooling rate in a temperature range from -50°C up to 150°C.

Results and Discussion

Feasibility area of the SHS ignition is plotted in the upper part of Figure 1. A minimum amount of energy is required to get propagating reaction: the conditions with energy lower than 80 J, i.e. of 150 W and 0.4 s and of 100 W and 0.6 s, did not propagate and no porous NiTinol was fabricated. Analyses were consequently performed only on porous reacted samples, which were produced in the range of ignition energy from 80 J up to 180 J.

It was observed that in some samples large pores, passing through the entire cross section of the specimen, were formed. For the sample obtained with 200W for 0.4s, longitudinal discontinuity between upper and lower part of the sample was seen. The energy provided during ignition affected

the upper part of the sample leading to unstable reaction condition, promoting the formation of big and elongated pores close to the ignition area. The porosity obtained in the range 42-48% was not clearly affected by the investigated process parameters.

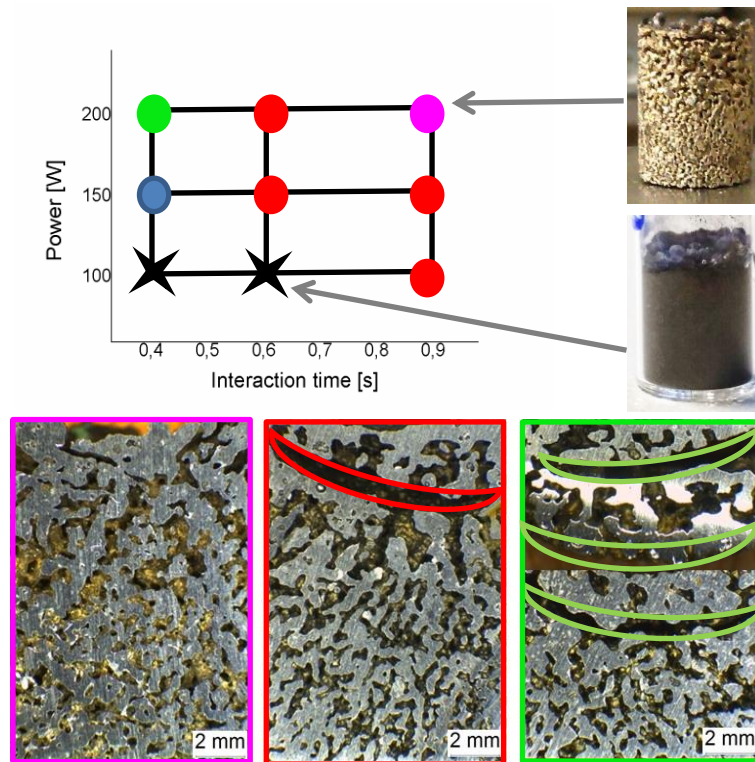


Figure 1: Feasibility area of laser ignition: circles and crosses for reacted (b) and unreacted (c) samples respectively. In the lower part longitudinal section of reacted samples having different porosity paths.

In DSC curves of all analyzed specimens the martensitic transformation is clearly observable and does not depend on the parameters (see Figure 2). The average values of the transformation temperatures M_s , M_f , A_s and A_f are 69, 50, 86 and 109°C and the heats exchanged upon cooling and heating are 7.3 and 7.7 J/g respectively. The measured values of enthalpy are about half of the value of a fully annealed bulk NiTi and roughly comparable to slightly deformed NiTi.

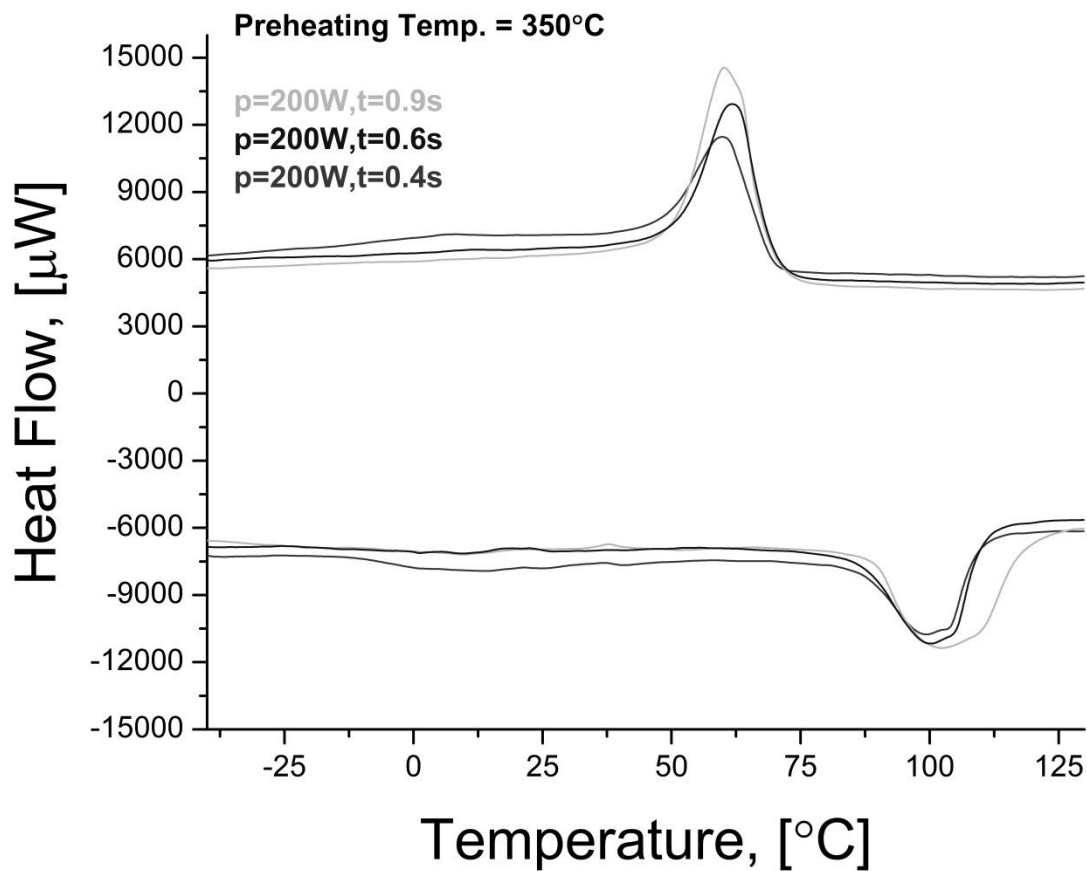
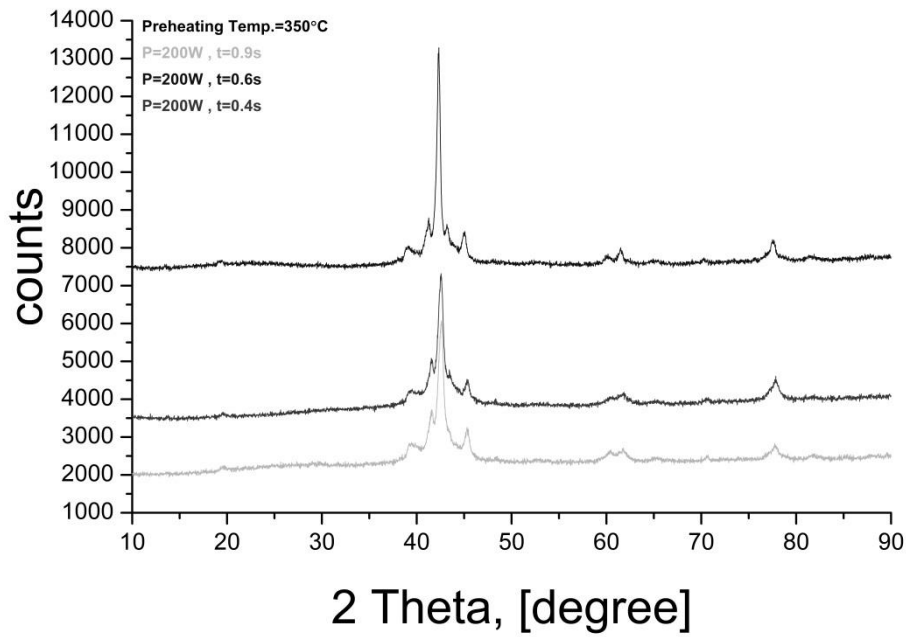
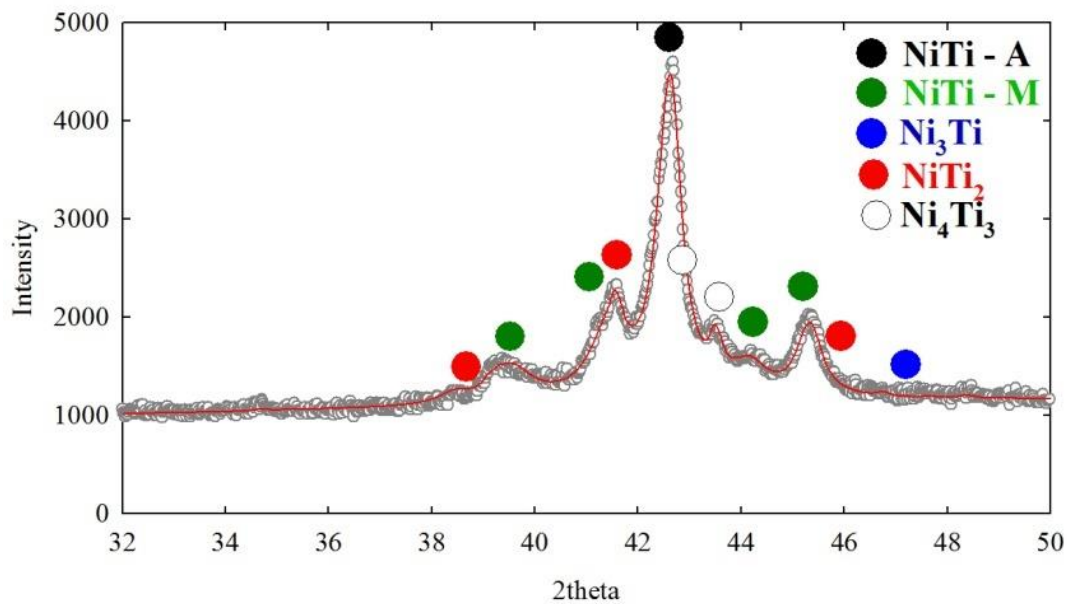


Figure 2: DSC scans of porous NiTi samples produced varying interaction time

In Figure 3 XRD spectra of samples produced with 200W are shown. No evident variation of the phases was detected changing the process conditions (see Figure 3a): this is in good agreement with the DSC results. According with Rietveld refinement (see Figure 3b), martensite and austenite were estimated about 52% and 40% respectively while the secondary phases NiTi_2 , Ni_3Ti and Ni_4Ti_3 were present in trace (3.5%, 0.5% and 4% respectively). The amount of martensite is in good agreement with the DSC enthalpy values.



(a)



(b)

Figure 3: Complete XRD spectra at varying the process conditions (a); identification of the phases in a limited 2θ range (b).

The microstructure of the samples was analyzed observed using SEM-EDX. In the non homogeneous-medium grey matrix, three main microstructures were observed: dark branched phase, light grey polygonal phase, and close to the latter, a smaller light grey globular and acicular phase, as shown in Figure 4. EDX analysis confirms the presence of the four compounds identified from XRD analysis.

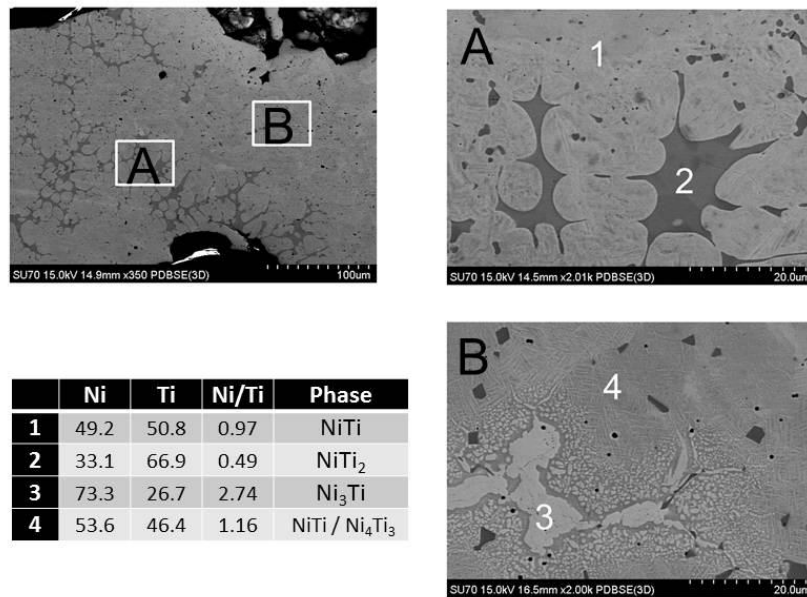


Figure 4: SEM pictures of different areas present in porous NiTi sample (150W; 0.6s). In the inset, EDX results for the different points.

In most regions of the samples, the matrix was distinctly characterized by two different grey shades: EDX analyses revealed that the darker one was characterized by nearly stoichiometric composition, hence leading to NiTi phase that present martensitic structure at room temperature, whilst the brighter regions are characterized by Ni-rich composition, thus supporting the XRD observation of NiTi-austenite. The presence of NiTi₂ (dark phase) and Ni₃Ti (polygonal bright phase) was confirmed from EDX measurements. It was not possible to analyze directly the composition of acicular phase, but composition of this area was far less rich in Ni than the latter ones, supporting the identification as Ni₄Ti₃ mixed with NiTi matrix.

Conclusions

In this work the effect of laser power and interaction time on porosity, microstructure and calorimetric properties of porous NiTiInol samples, produced through laser ignited SHS, was studied. It can be summarized as follows:

- Laser ignition can affect the propagation front, that led to the formation of gaps and big elongated pores inside the samples, leading to different porosity morphologies by changing the input energy under unstable condition.
- The feasibility area of ignition was defined from laser power and interaction time for producing Nitinol samples with 42-48% porosity.

- All samples showed the presence of several phases, not influenced from the process parameters.
- Calorimetric analysis showed that phase transformation is present in all the samples and the temperatures are not affected by the investigated process parameters.

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